OAK RIDGE National Laboratory

Deep Dive into the Oxygen Anion Redox in Na Layered Oxide Cathodes Synthesized by Eutectic

OE Peer Review Meeting

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Oak Ridge National Laboratory

ORNL is managed by UT-Battelle, LLC for the US Department of Energy

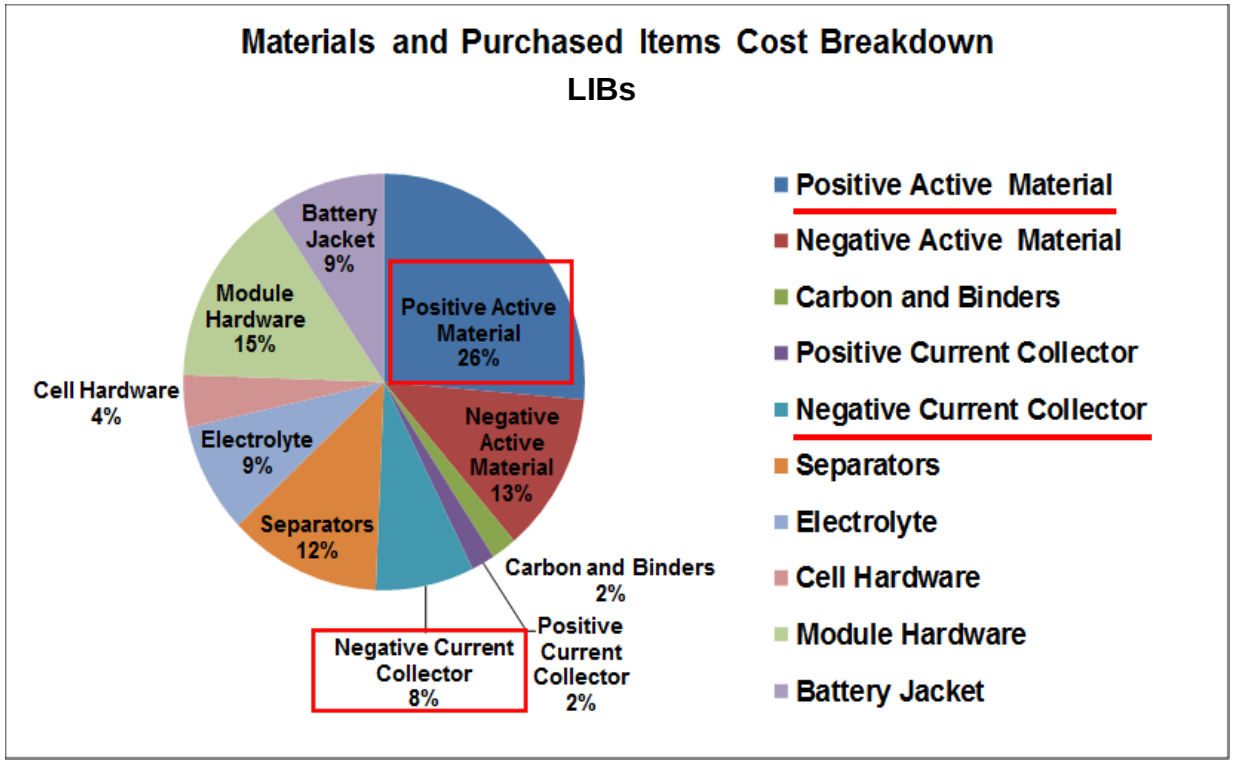
U.S. DEPARTMENT OF ENERGY

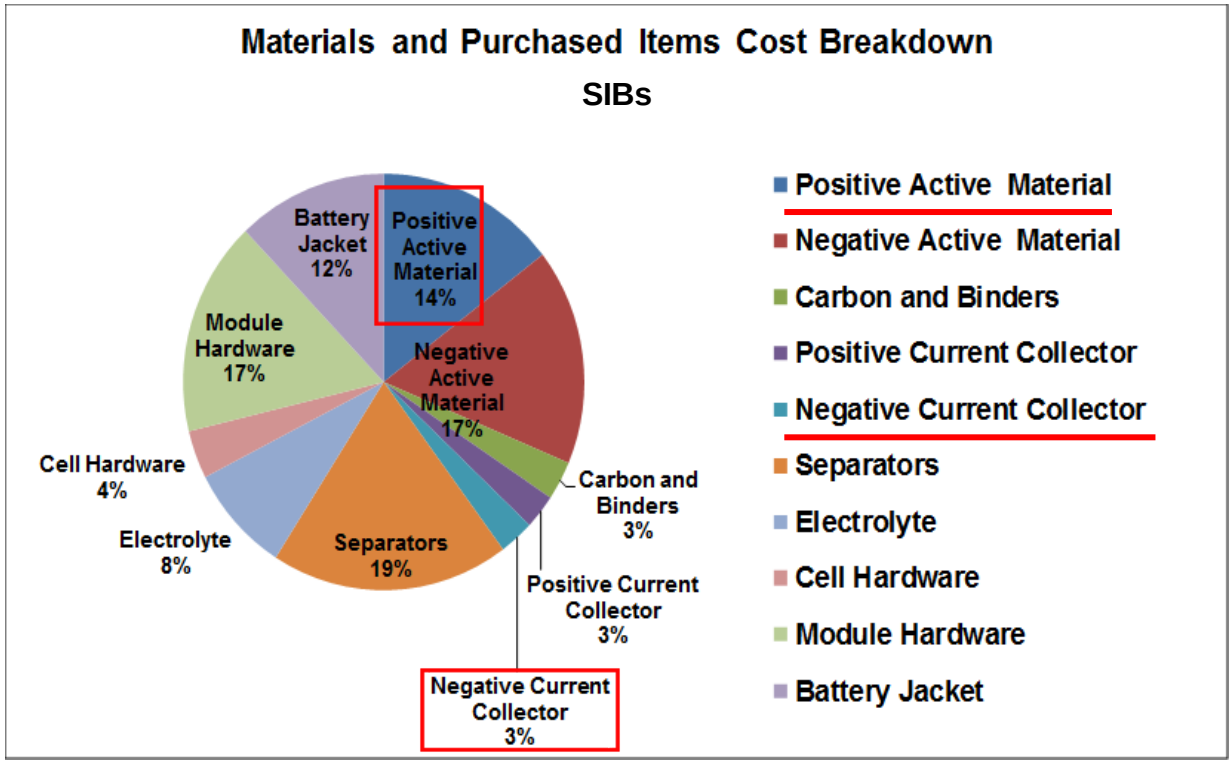
Why Na-Ion Batteries?

	Abundance in earth crust (ppm)
Lithium	20 (rank 32nd)
Sodium	27500 (rank 6th)

For cost analysis (in 53 kWh battery pack)

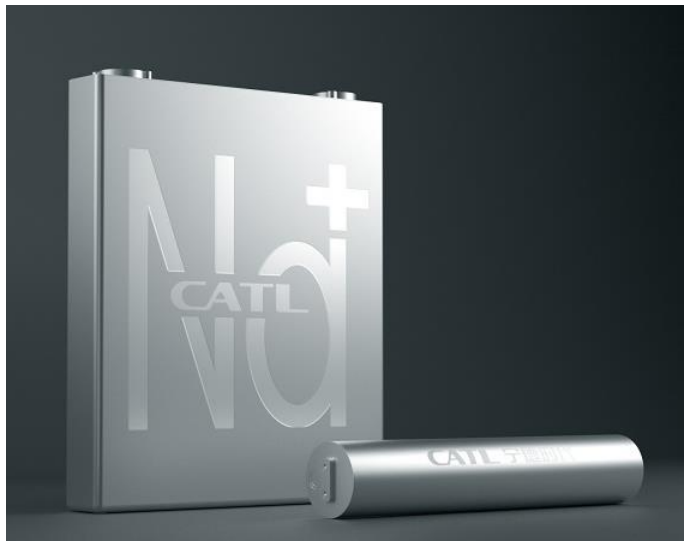
- Li-ion Batteries (LIBs):
  NMC622 vs. graphite
- Na-ion Batteries (SIBs):
  $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ vs. hard carbon





Li et al, ***Energy Storage Materials,*** 25 (2020) 520–536.

CATL's First Generation Na-ion Battery Released in 2021



https://www.catl.com/en/news/665.html

- Cathode: Prussian white with re-designed bulk structure
- Anode: Hard carbon
- Cell energy density: 160 Wh/kg (with a goal of >200 Wh/kg for the next generation)

Claimed performance to exceed current Li-ion battery technology:

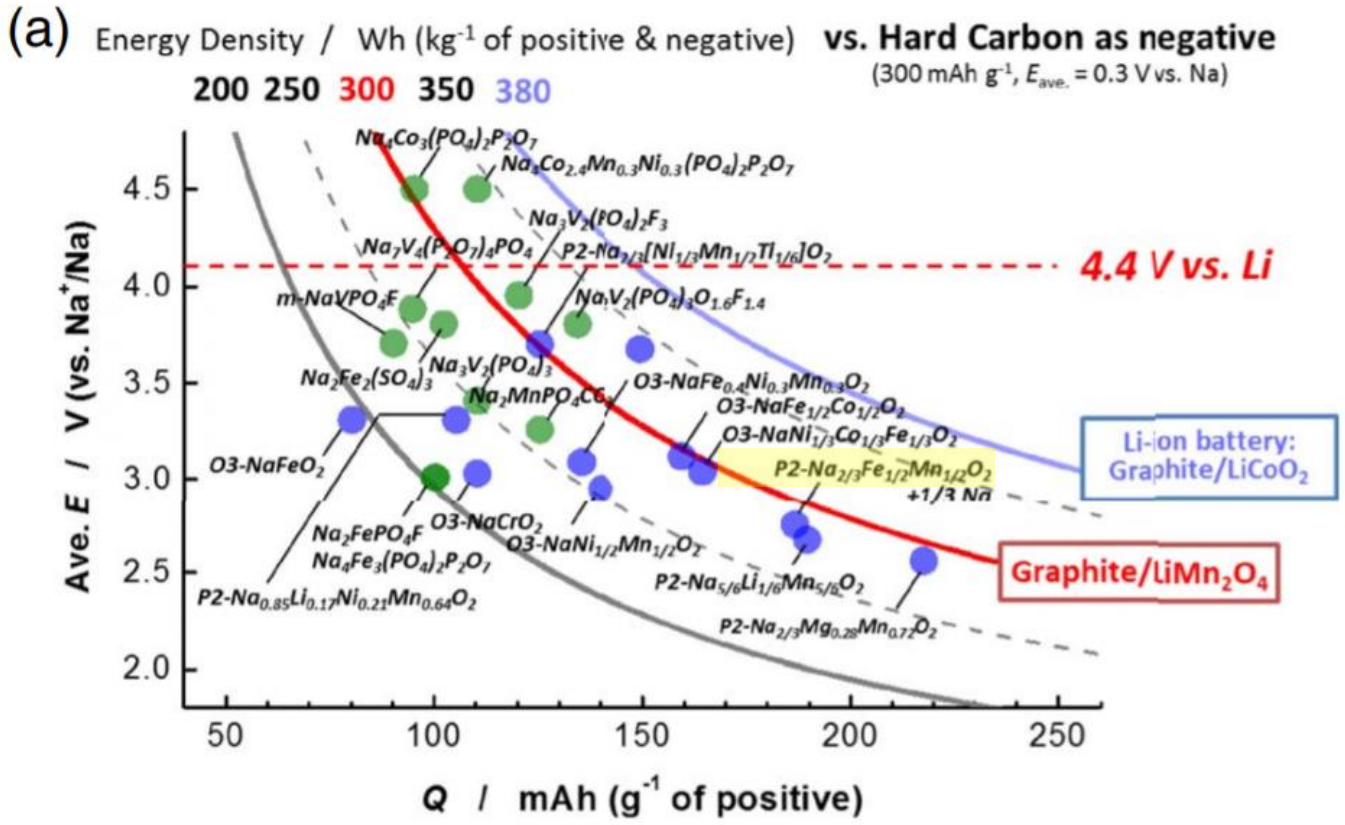
- 15 min charging to 80% SOC
- Capacity retention > 90% at -20 ºC

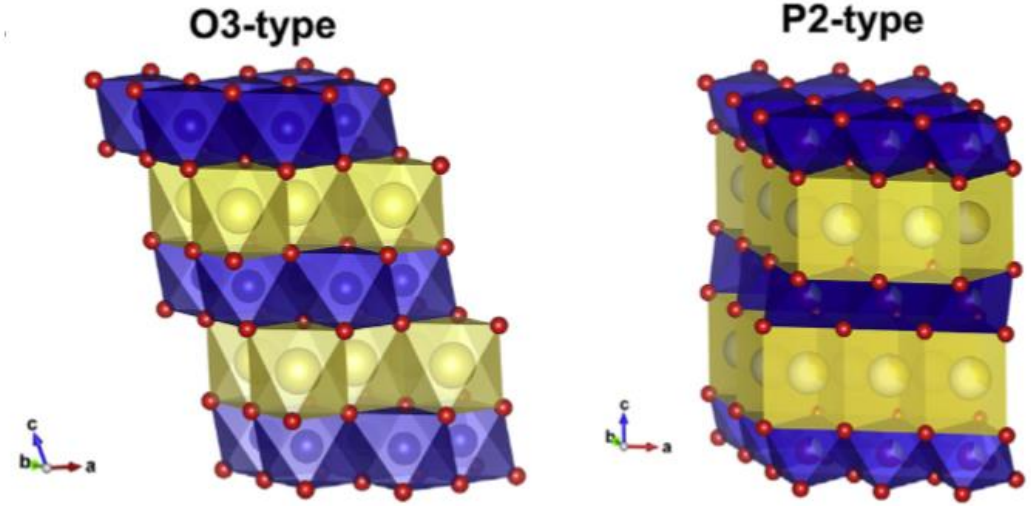
Commercialization of Na-ion batteries could take place sooner

The goal is not to substitute LIBs with SIBs but integrate them together to maximize performance for different working conditions

ORNL's Focus on Low-Cost Na Layered Transition-Metal Oxide Cathodes

Journal of The Electrochemical Society, 2015, 162, A2538.





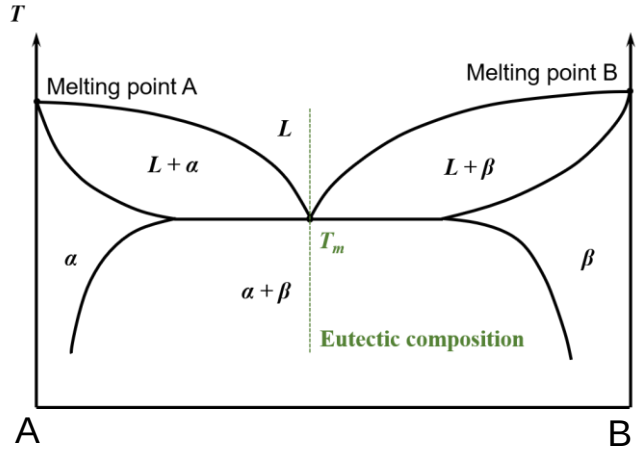
Li et al., ***Energy Storage Materials*** 25 (2020) 520–536.

	O3	P2
C-spacing	large	small
Stability upon charge/discharge	low	high
Voltage	high	low

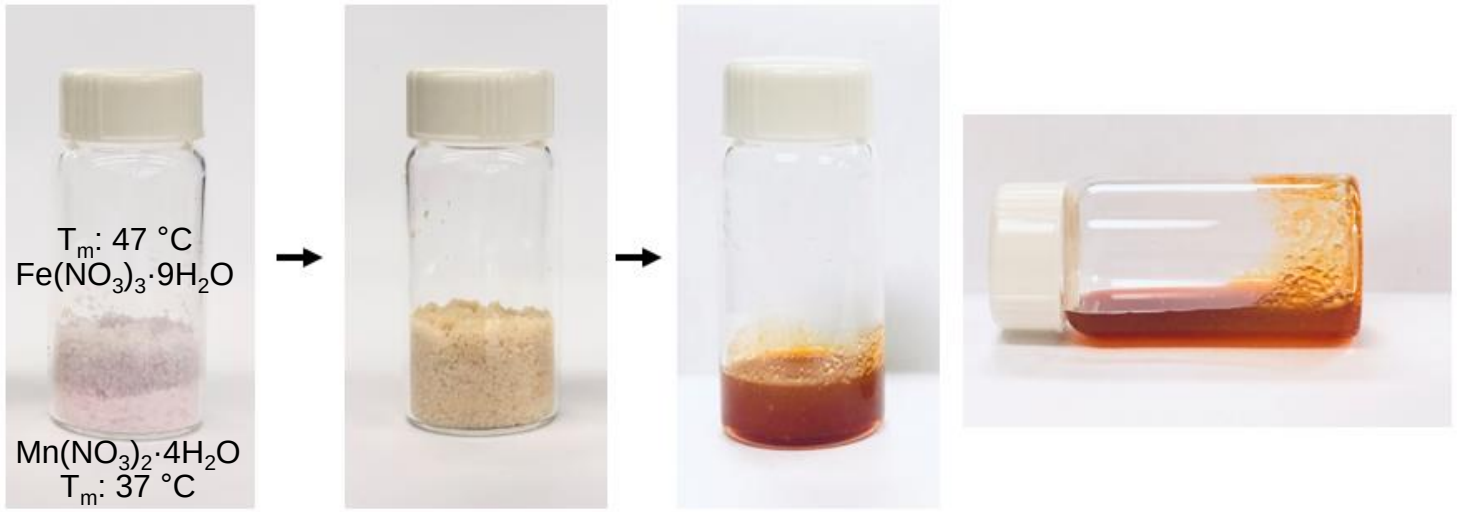
- **Theoretical capacity of P2-$Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$: 260 mAh/g**
- **Fe, Mn are both low-cost and abundant TM elements.**

ORNL's Eutectic Synthetic Approach Versus Conventional Synthesis of Sodium Transition Metal Layered Oxides

- Conventional synthesis – "Solid-state" & "Sol-gel" methods: Energy intensive and time-consuming mixing process + Impurity phases + Inhomogeneous particle size/morphology.
- **New approach: <u>Eutectic Synthesis</u> Developed at ORNL**



An example of $Na_xFe_{1/2}Mn_{1/2}O_2$ – Precursors: transition metal nitrates



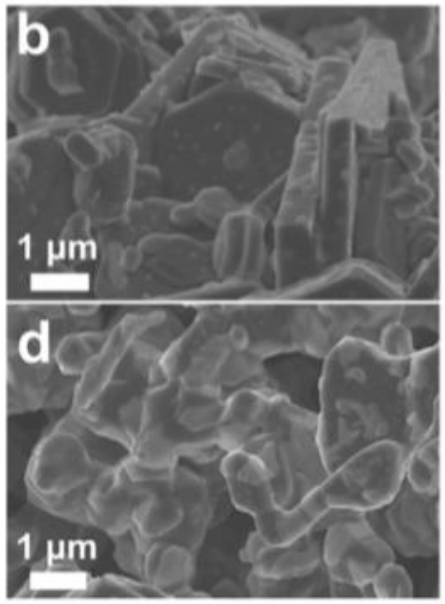
From metal nitrates precursors to liquid eutectic formation in <u>0.5 hr</u>

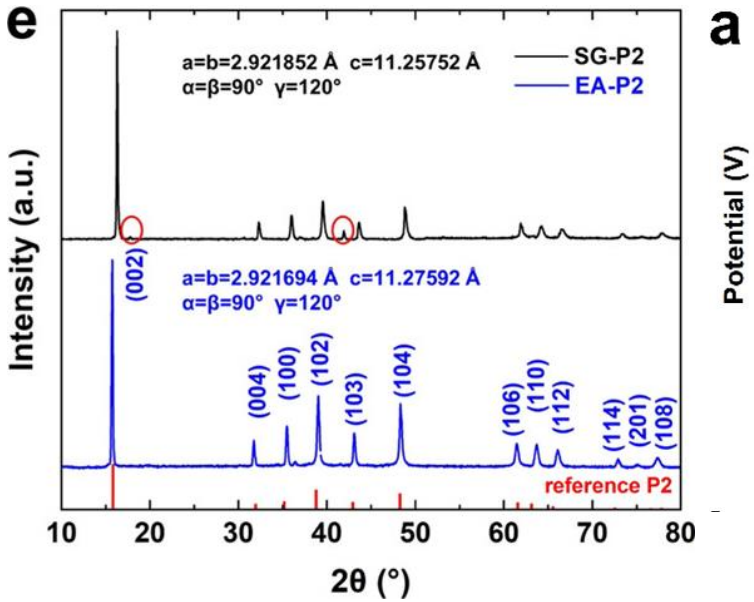
Eutectic Synthesis

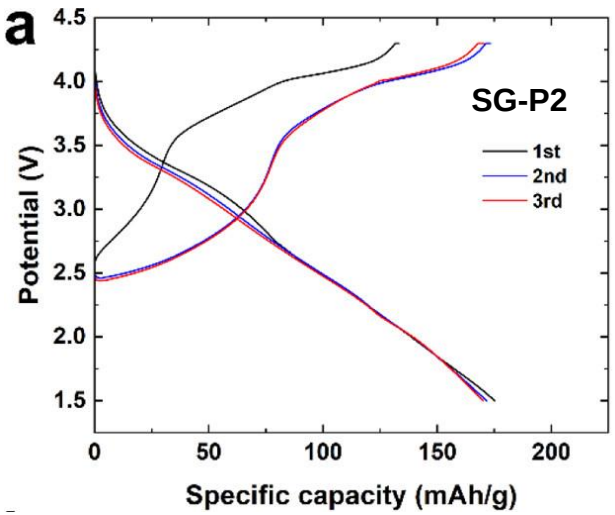
- <u>Mechanism</u>: liquid eutectic alloy formation.
- <u>Advantages</u>: uniform liquid-based mixing down to the atomic level; applicable to a variety of TM oxides with tunable composition; higher crystallinity; homogeneous morphology; fast processing.

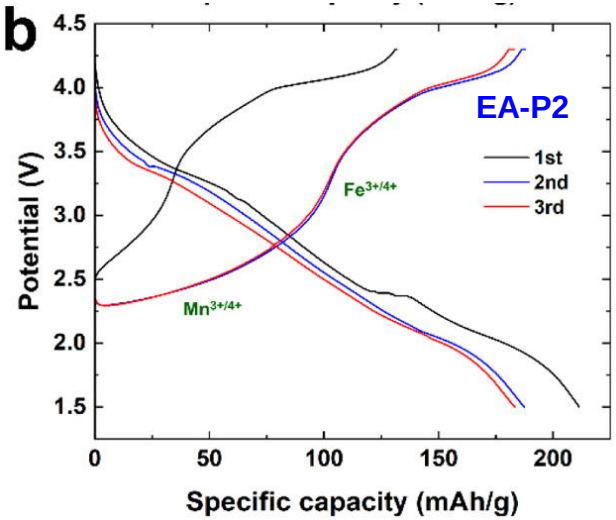
$Na_xFe_{1/2}Mn_{1/2}O_2$ Synthesized by Eutectic vs. Sol-Gel Method

SG-P2





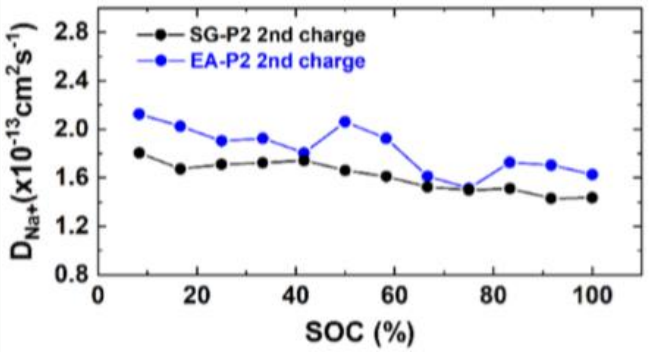


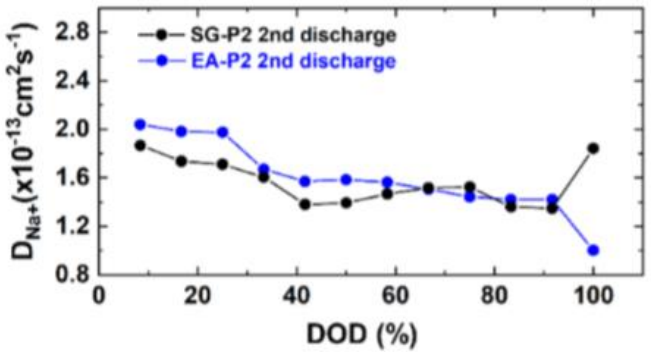


Higher specific capacity

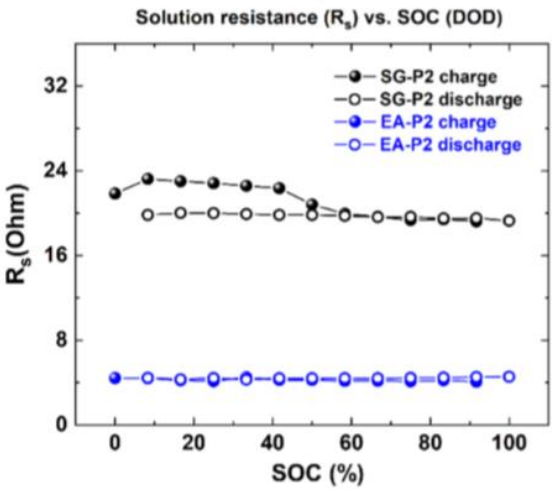
EA-P2

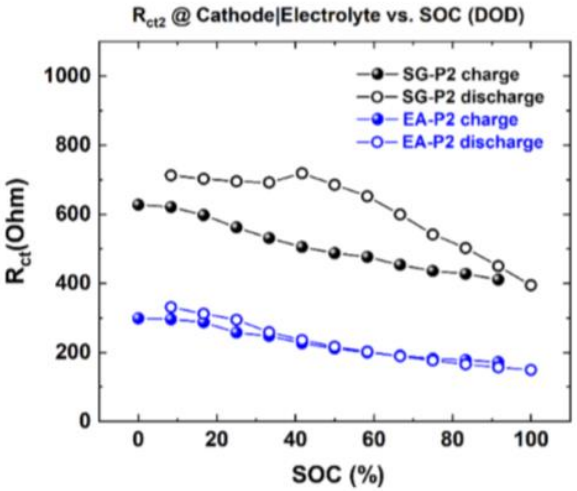
Better morphology and crystallinity





Faster kinetics





Lower interfacial resistance

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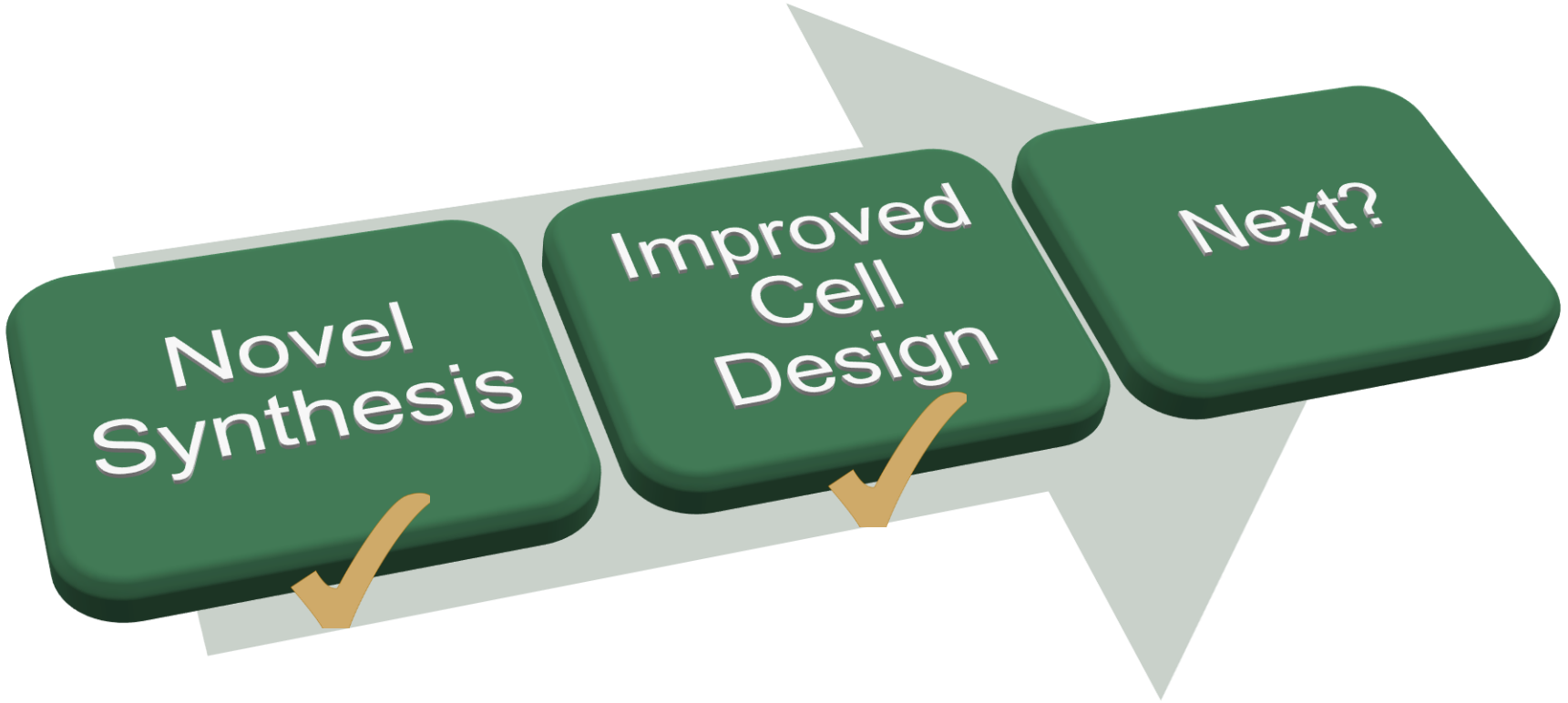
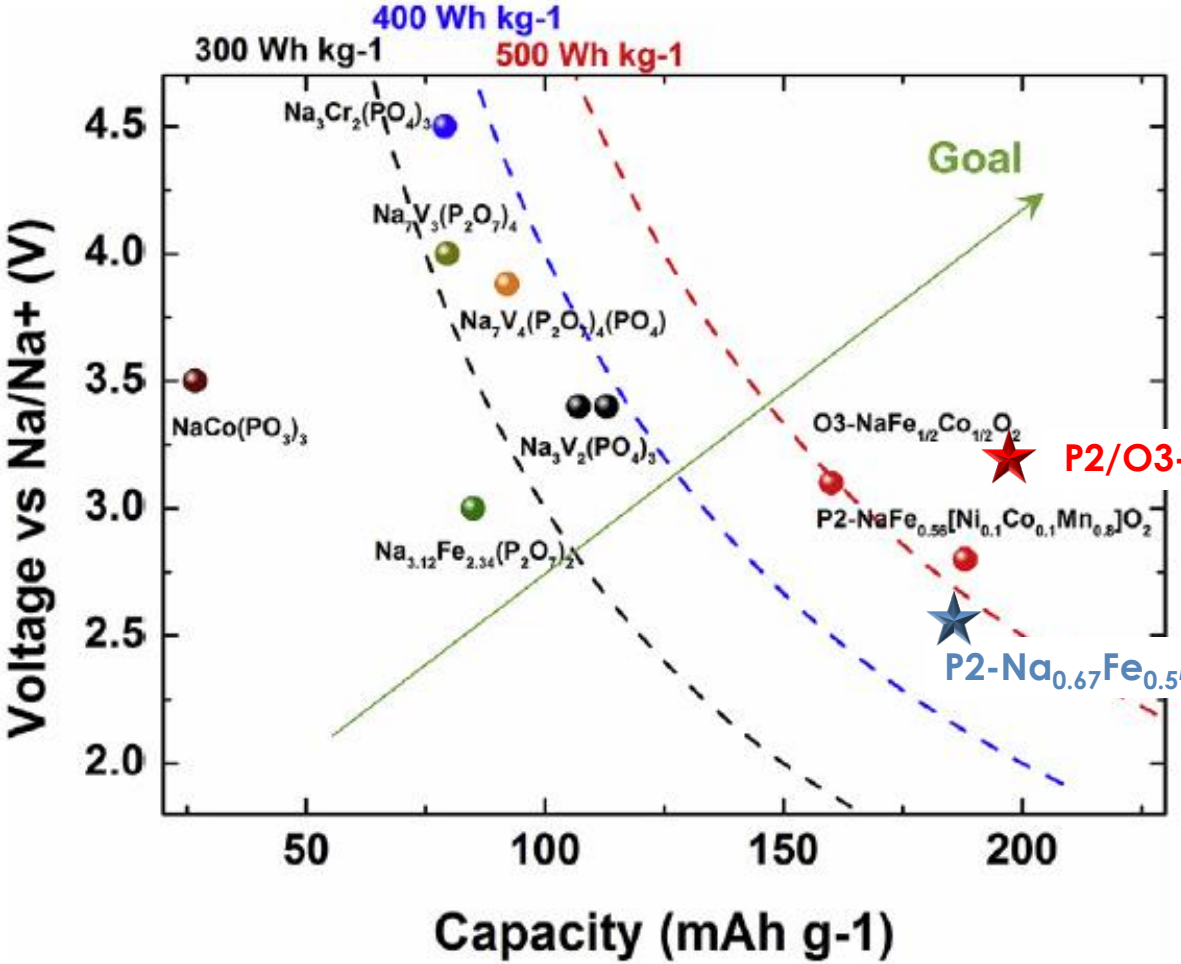
Li et al., ***ACS Appl. Mater. Interfaces*** 2020, 12, 23951−23958.

Sodium Layered Transition Metal Oxide Cathode



Shifting Towards Cathodes with Higher Voltage



Cobalt-free

P2/O3-$Na_xNi_{0.5}Mn_{0.5}O_2$

- For potential high-energy applications, SIB cathodes with higher voltage and higher capacity are preferred.
- From the cost-perspective, cobalt-free cathodes are preferred.

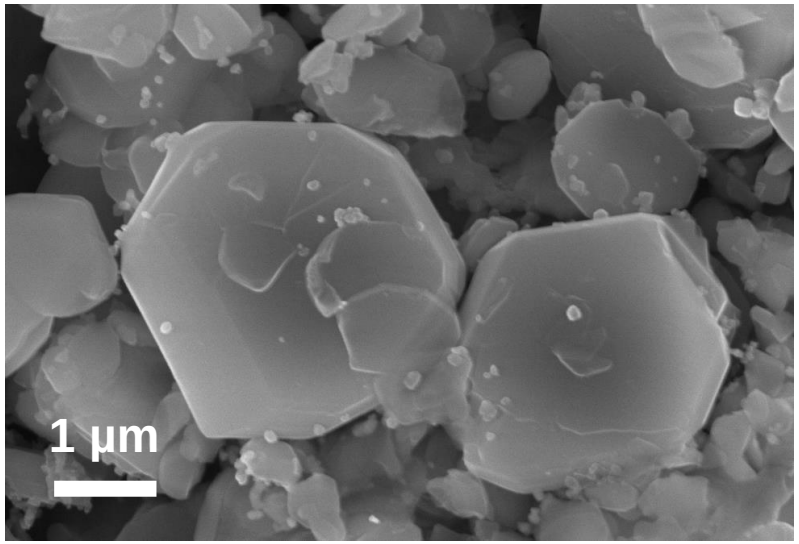
Li et al., ***Energy Storage Materials*** 25 (2020) 520–536.

Eutectic Synthesis of P2/O3-$Na_xNi_{0.5}Mn_{0.5}O_2$

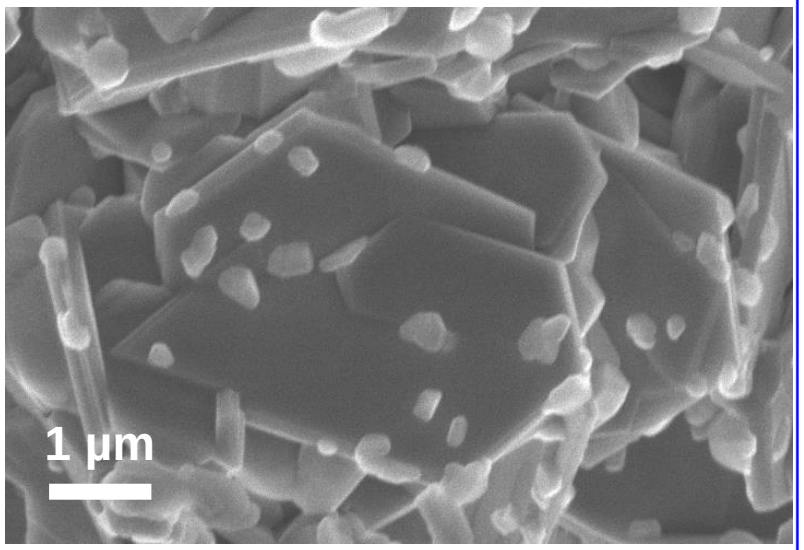
Na deficient

Na rich

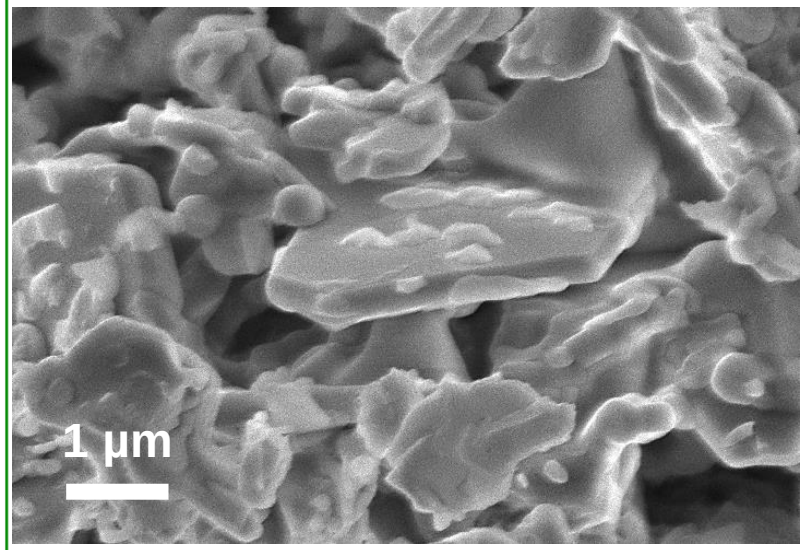
$Na_{0.64}Ni_{0.5}Mn_{0.5}O_2$

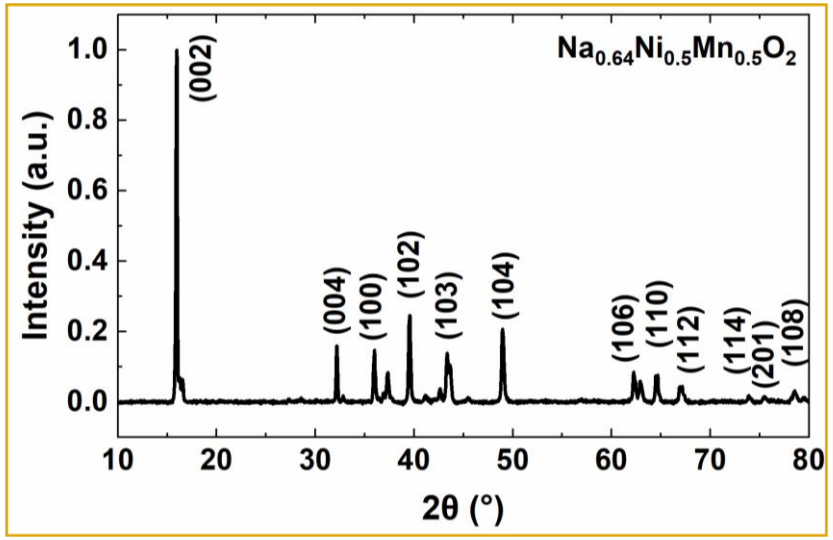


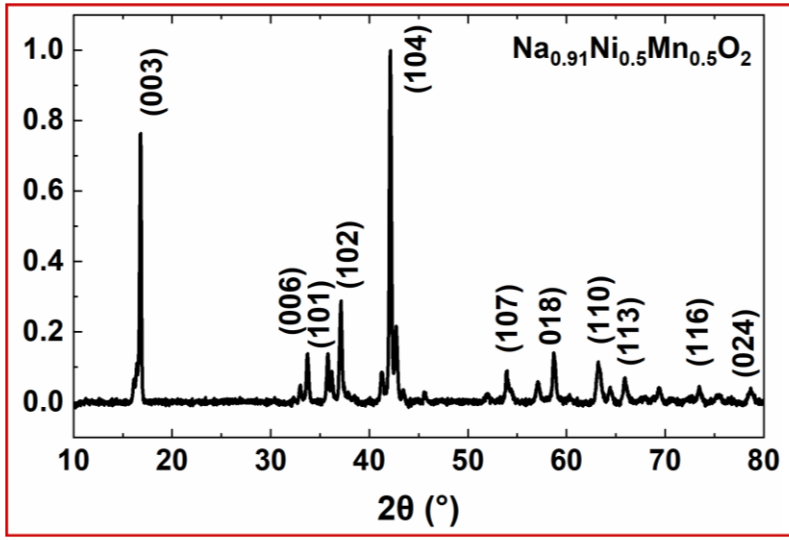
$Na_{0.91}Ni_{0.5}Mn_{0.5}O_2$

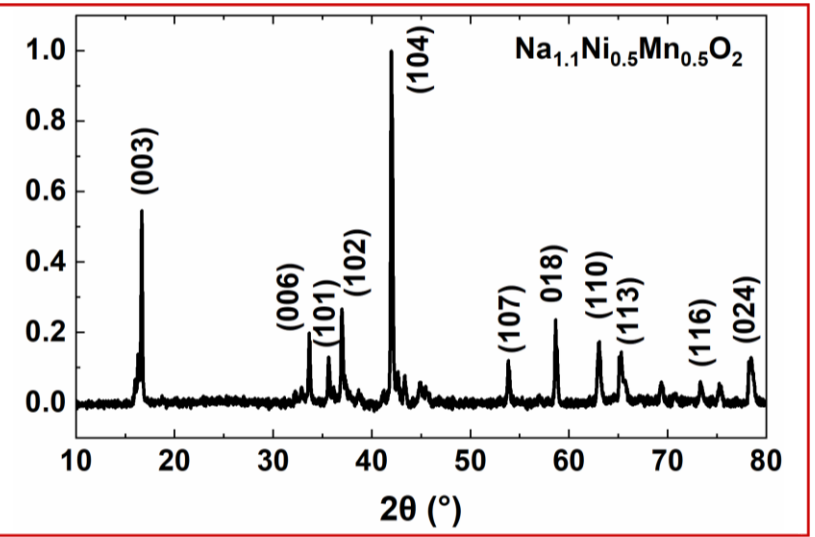


$Na_{1.1}Ni_{0.5}Mn_{0.5}O_2$









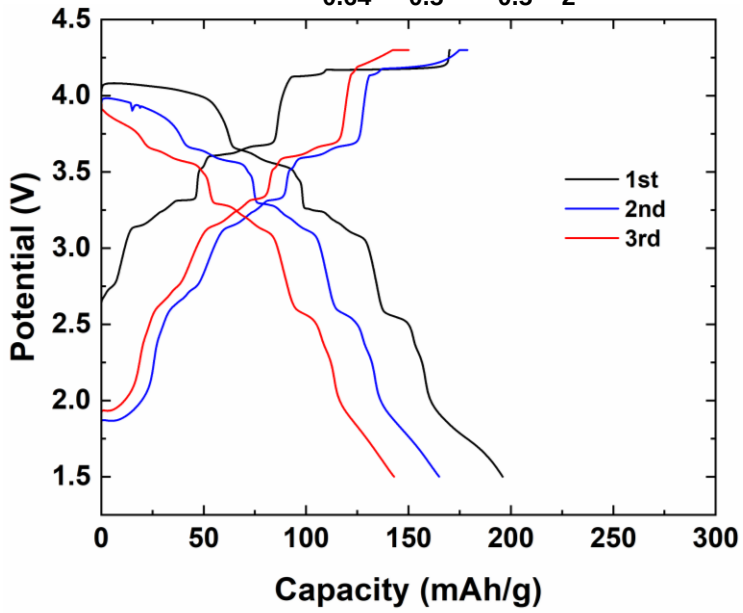
P2 phase

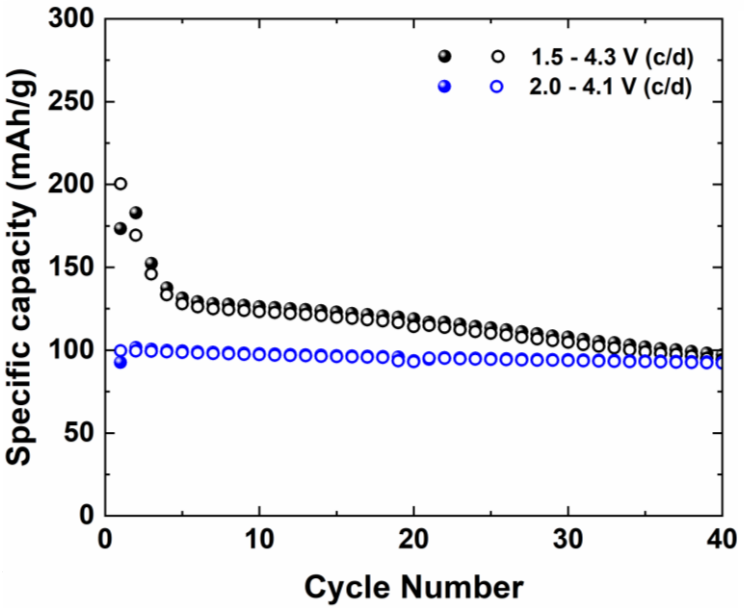
O3 phase

Li et al, *in preparation.*

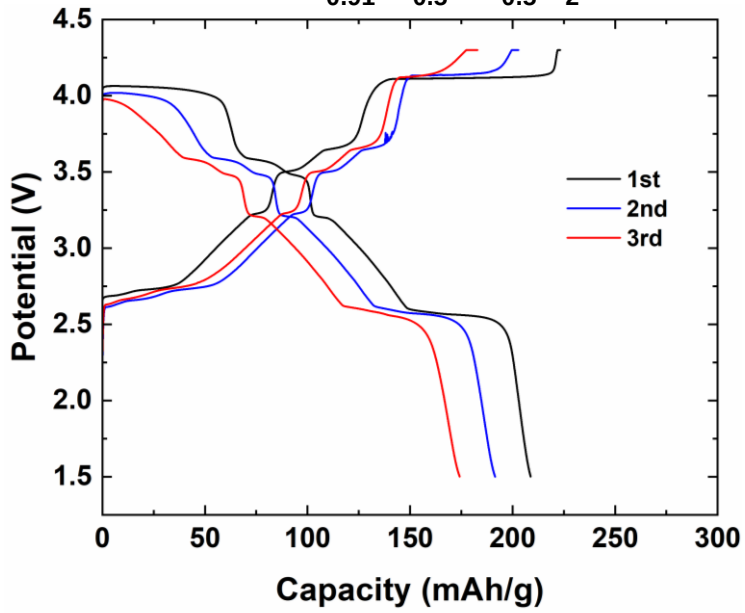
Electrochemical Performances of P2/O3-$Na_xNi_{0.5}Mn_{0.5}O_2$ Half Cells

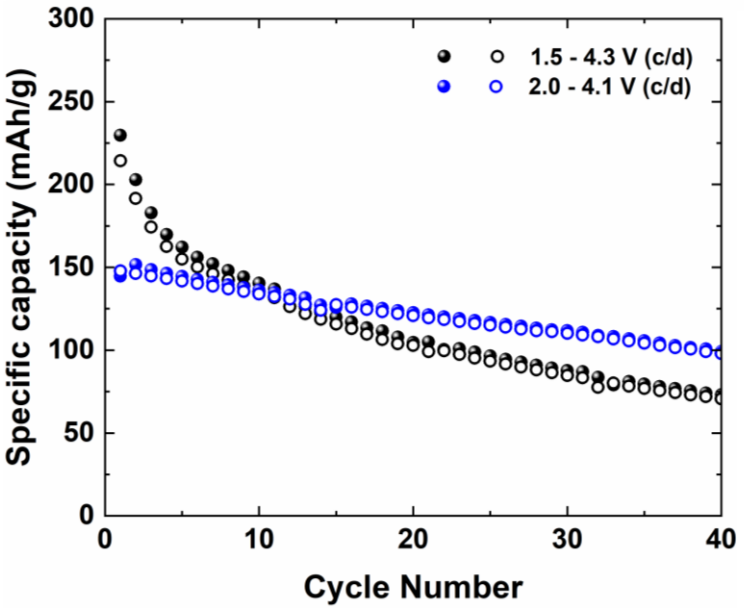
P2-$Na_{0.64}Ni_{0.5}Mn_{0.5}O_2$



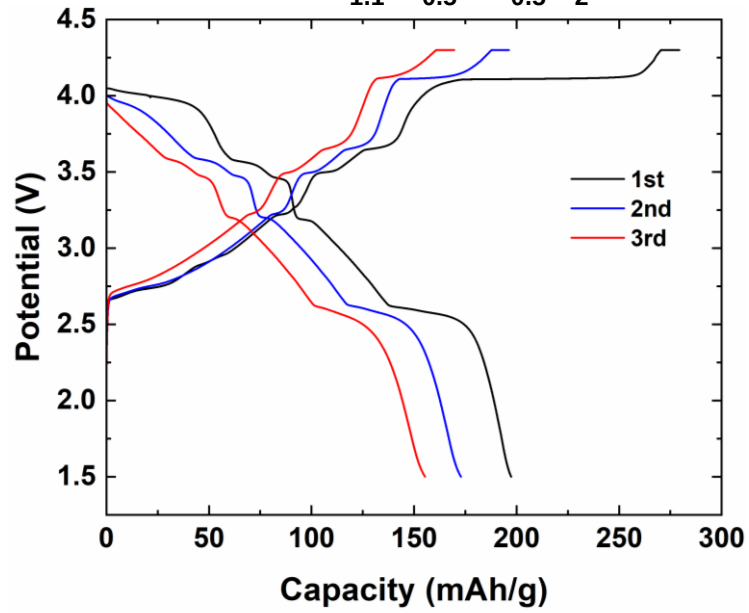


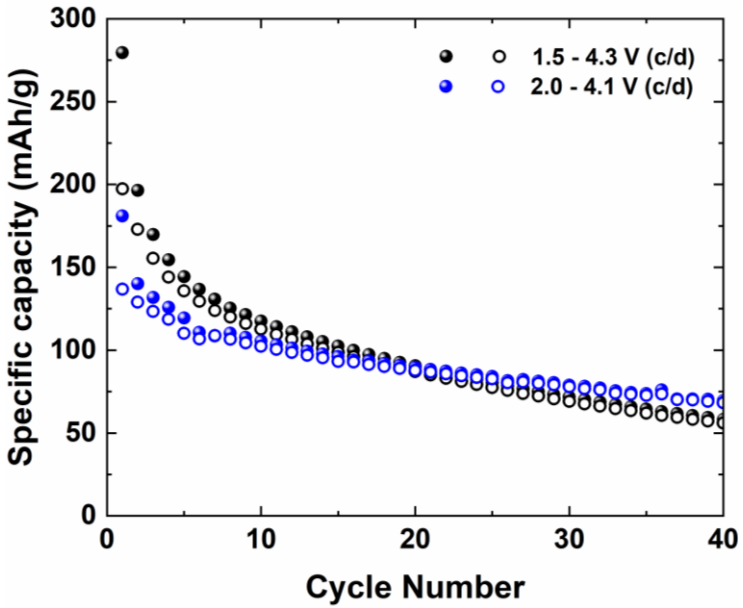
O3-$Na_{0.91}Ni_{0.5}Mn_{0.5}O_2$





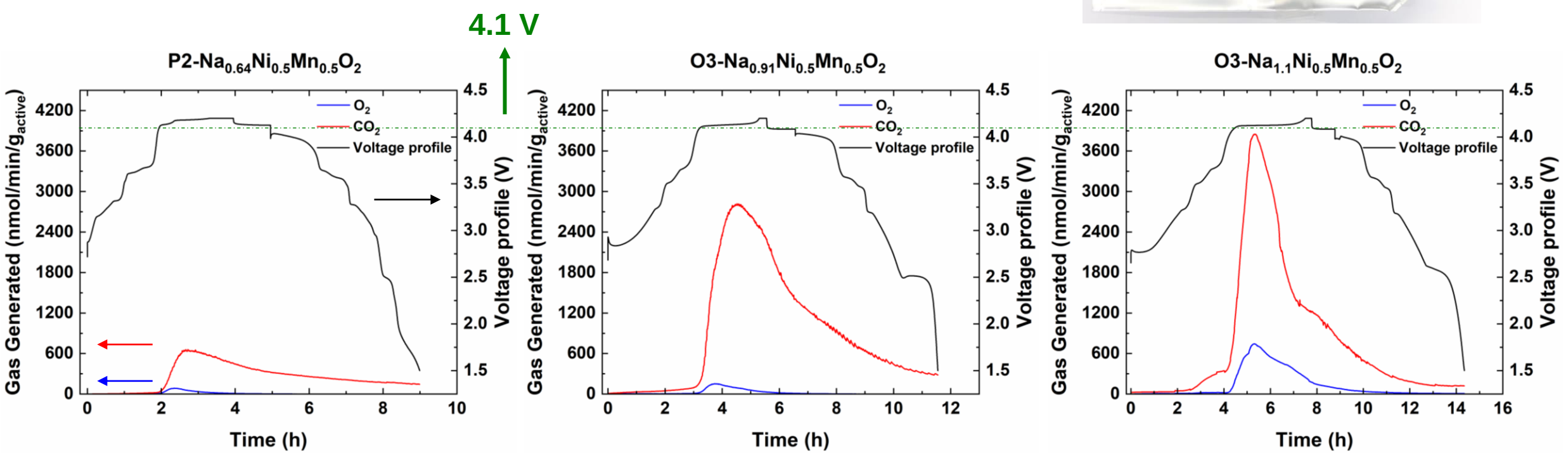
O3-$Na_{1.1}Ni_{0.5}Mn_{0.5}O_2$





In-situ Gas Analysis to Understand the Initial Capacity Fading

- In-situ gas analysis (GC-MS) was performed on single layer pouch cells incorporated with gas outlet connecting to the mass spectrometer.



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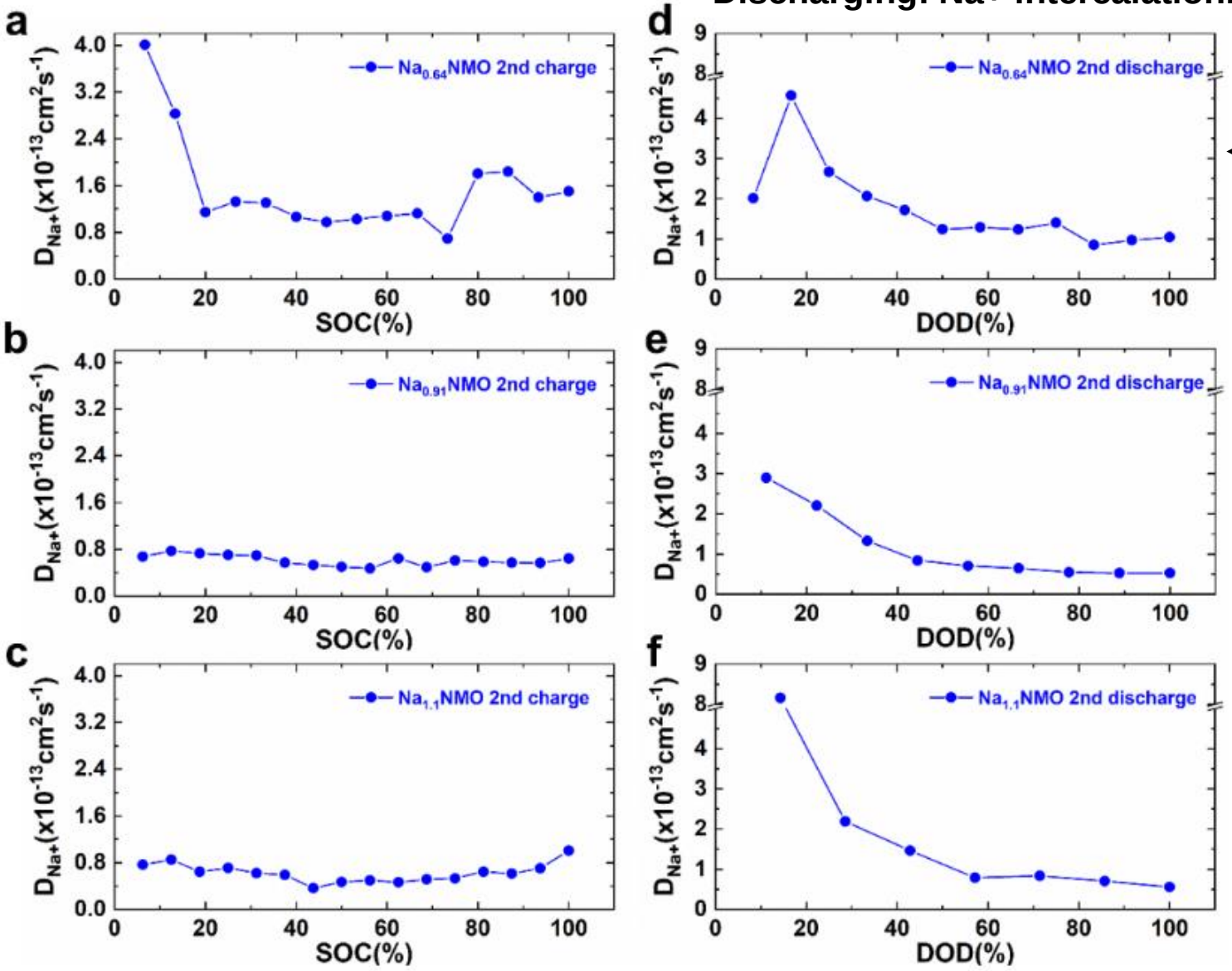
Li et al., In preparation

Na^+ Diffusion Kinetics & Understanding of Structural Changes by Operando XRD

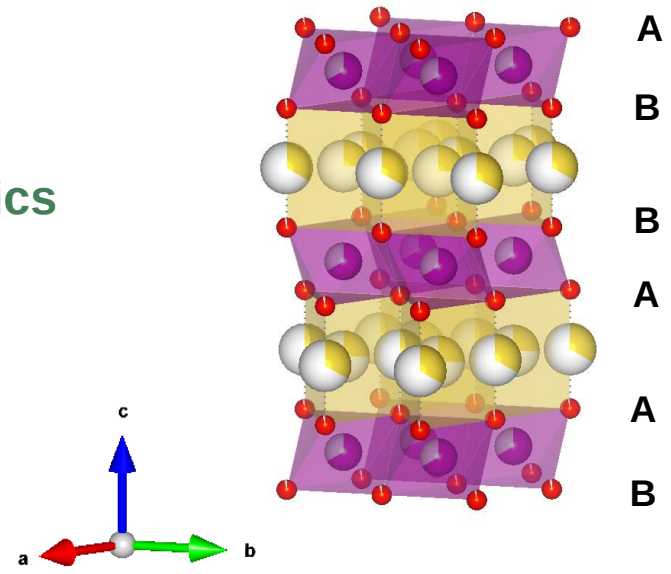
Charging: Na^+ extraction & Oxygen anion redox.
Discharging: Na+ intercalation.

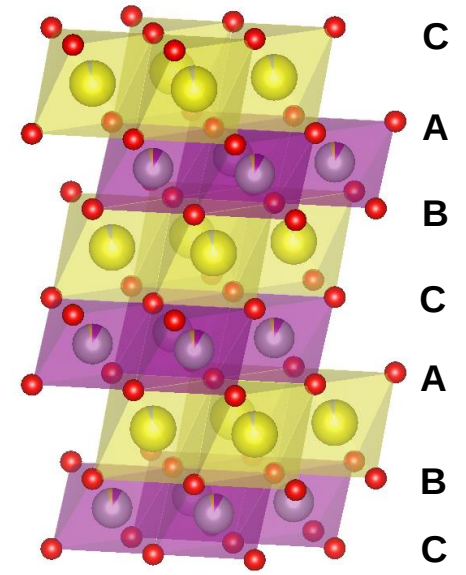


← Fast kinetics

Slightly slower kinetics

P2-type

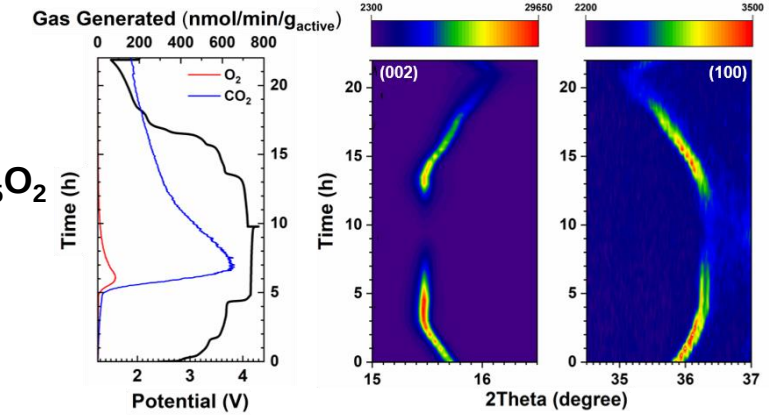


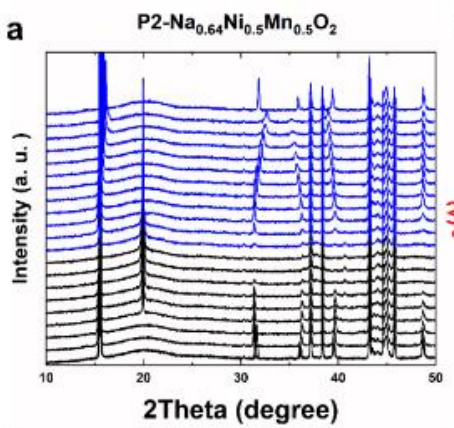


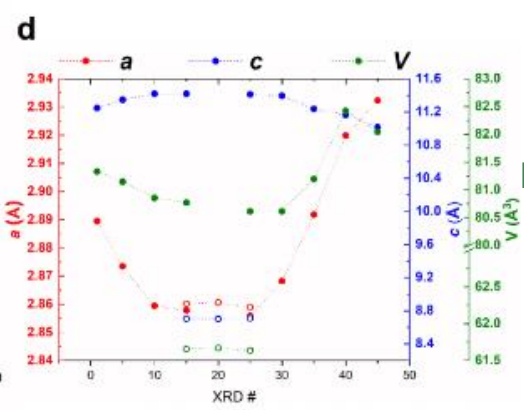
O3-type

Operando XRD Reveals Differences in Structural Changes

P2-$Na_{0.64}Ni_{0.5}Mn_{0.5}O_2$

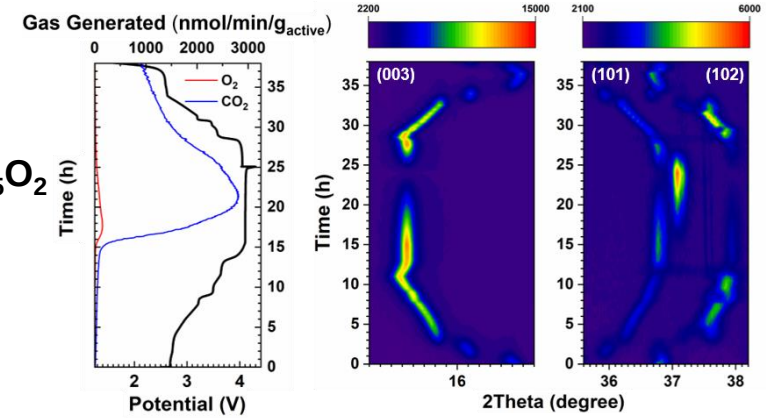


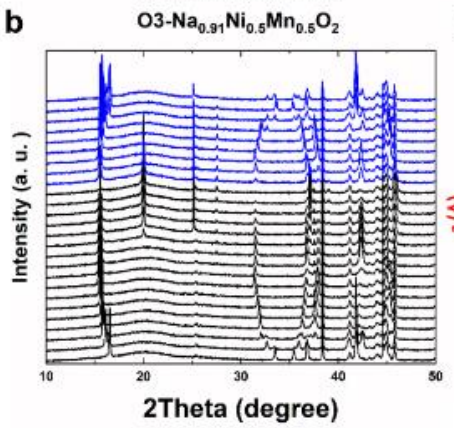


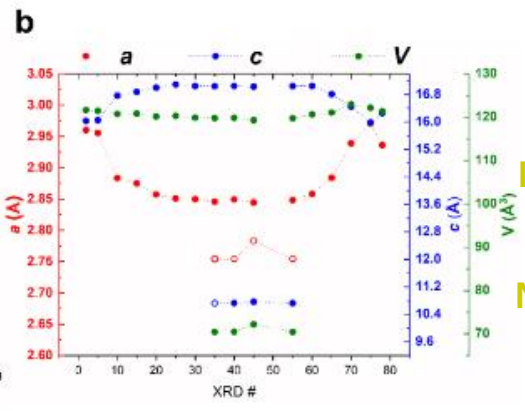


Less volume change
More reversible
phase transition

O3-$Na_{0.91}Ni_{0.5}Mn_{0.5}O_2$

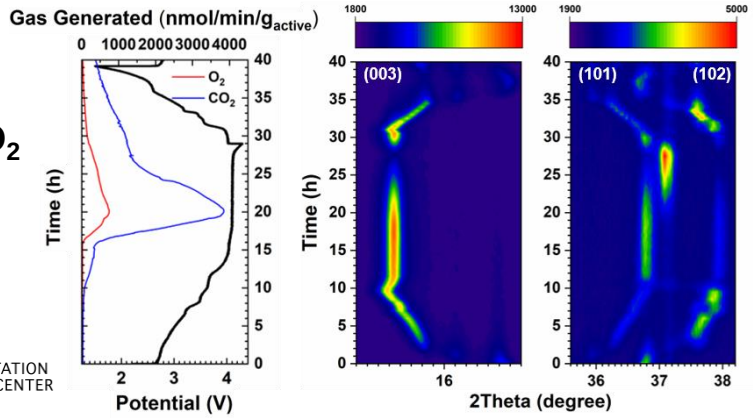


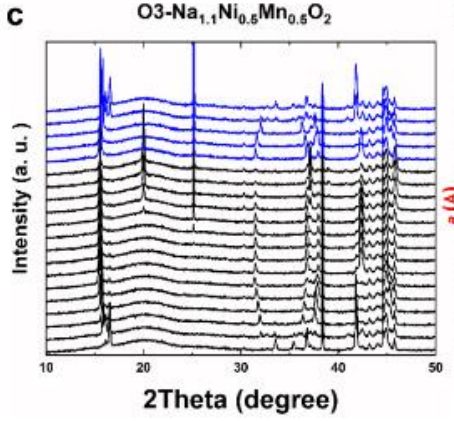


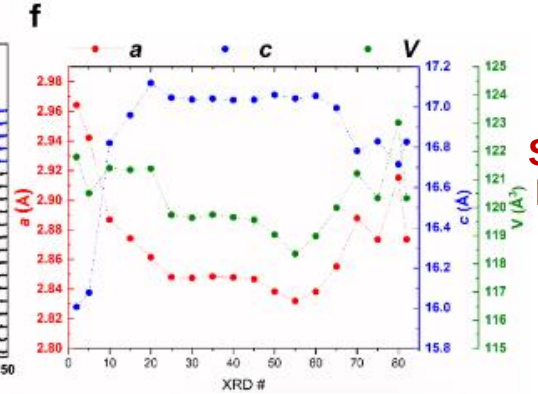


More volume change
Less reversible
phase transition
New phase formation

O3-$Na_{1.1}Ni_{0.5}Mn_{0.5}O_2$



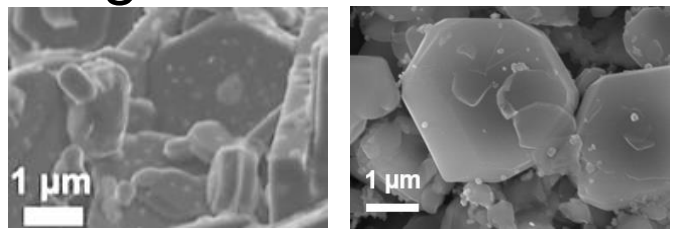




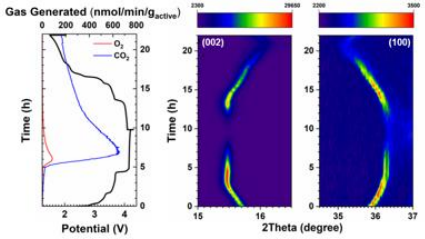
Severe volume change
Less reversible phase
transition
New phase formation

Summary

- We have demonstrated ORNL's capabilities in synthesizing different kinds of Na transition metal layered oxides by eutectic method.



- We have performed in-depth analysis with the oxygen anion redox for transition metal layered oxide cathodes at high voltage.



- We have envisioned future cathode materials design by stabilizing surface and bulk structure of transition metal layered oxide cathodes .

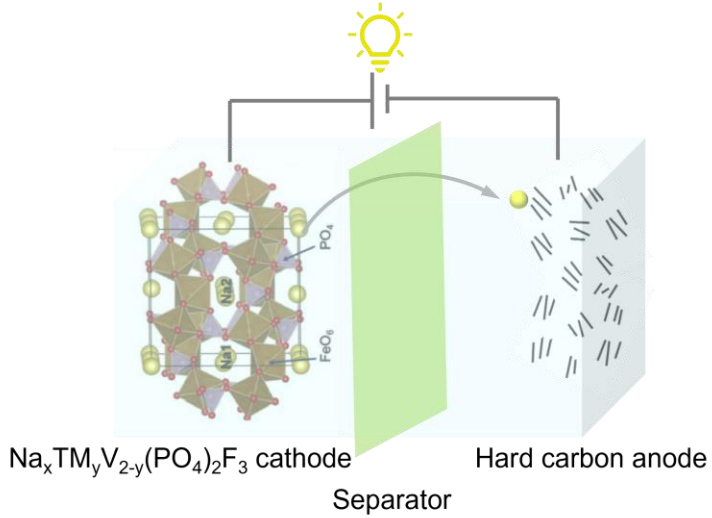
FY21 Achievements and FY22 Plan

FY2021 Accomplishments:

- Applied the ORNL team-developed novel eutectic synthesis method for Na transition-metal oxide layered materials with different compositions.
- In-situ gas analysis on pouch cells using $Na_xNi_{0.5}Mn_{0.5}O_2$ (x=0.64, 0.91, 1.1) cathodes for initial capacity fading mechanism study.
- Deep-dive into the reaction mechanism and structural evolution upon electrochemical charge/discharge assisted by advanced operando characterizations.

FY2022 Plan:

- New chemistry
  - Eutectic synthesis of new series of Na layered oxide cathodes.
  - Investigate another low-cost $Na_xTM_yV_{2-y}(PO_4)_2F_3$ cathodes.
- Cell deliverables
  - Continue the efforts in tackling the anode sodiation issue in pouch cell configuration.
  - Demonstrate ORNL's first generation Na-ion battery.



Publications and Invention Disclosure

- M Li, C Jafta, L Geng, J Liu, Y Bai, J Li, R Essehli, I Belharouak. Oxygen Anion Redox Activity Suppressed by Ribbon-Like In-Plane Cation Ordering in NaxNi0.5Mn0.5O2 Cathodes. *In preparation*.
- R. Essehli, R. Amin, A. Abouimrane, M Li, H ben Yahia, K Maher, Y Zakaria, I Belharouak. Temperature-dependent Battery Performance of a Na3V2(PO4)2F3@MWCNT Cathode and In-situ Heat Generation on Cycling, *ChemSusChem*, 2020, 13, 5031-5040.
- M. Li, DL. Wood, Y. Bai, R. Essehli, MR. Amin, CJ Jafta, N Muralidharan, J Li, I Belharouak. Eutectic Synthesis of P2-Type NaxFe1/2Mn1/2O2 Cathode with Improved Cell Design for Sodium-Ion Batteries. *ACS Applied Materials & Interfaces*, 2020, 12, 23951-23958.
- M. Li, Z Du, MA Khaleel, I Belharouak. Materials and engineering endeavors towards practical sodium-ion batteries, *Energy Storage Materials*, 2020, 25, 520-536.
- M Li, Y Bai, D Wood, J Li. Synthesis of transition metal layered oxide materials via eutectic mixtures for sodium-ion battery cathodes

Acknowledgement

ORNL – Michael Starke and Thomas King, Jr.

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